

PHOSPHORUS-CONTAINING INORGANIC AND SEMIORGANIC POLYMERS

ABSTRACT

The synthesis of new phosphorus-containing polymers expected to have high thermal stability was the object of this research. Accompanying this effort has been a study of model compounds and prototype reactions, to obtain information on bond formation and bond stability.

Among phosphorus-containing compounds, those containing the P-C-P linkage have unusual thermal stability. For example, several methylene and phenylene bis diphenylphosphine oxides are stable to 425-450°C (797-842°F). For this reason, the preparation of P-C-P type polymers by addition and condensation reactions using a variety of monomers under widely varied conditions was attempted.

Fundamental studies of the chemistry of P-C compounds are described. Reorganization studies indicated that the C₆H₅-P bond is probably stable to at least 400°C.

Polymers of the polyamide type with phosphorus in the backbone are described. Some prepared from a bibenzimidazole were stable to 425-450°C. (797-842°F), albeit of low molecular weight. Model compounds containing the phosphorus-imidazole bond showed stabilities as high as 500°C. (932°F.).

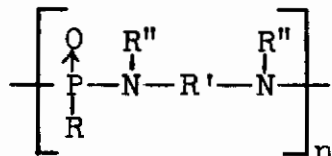
PART I. CONDENSATION POLYMERS FROM DIFUNCTIONAL PHOSPHORUS COMPOUNDS AND DIAMINES

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T. J. Morrow, Leo Parts, W. E. Weesner.

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INTRODUCTION

Polyamides containing phosphorus appeared to be a promising type of linear polymer containing the very stable PN bond. Reactions were therefore investigated which would yield polymers of the type



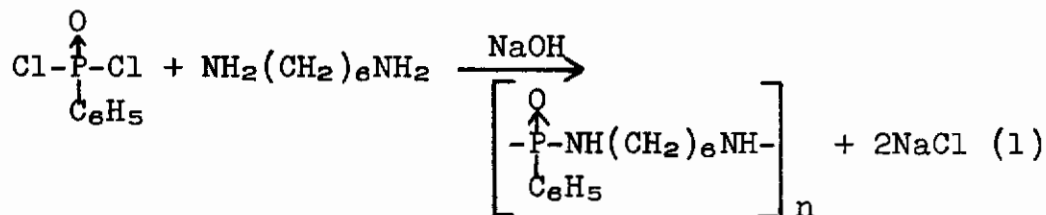
with the desired thermal stability to be obtained through selection of R, R' and R''.

Report Documentation Page			Form Approved OMB No. 0704-0188		
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 1962		2. REPORT TYPE		3. DATES COVERED 00-00-1962 to 00-00-1962	
4. TITLE AND SUBTITLE Phosphorus-Containing Inorganic and Semiorganic Polymers				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Paul V. Galvin Library, 35 W. 33rd Street, Chicago, IL, 60616				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
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15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 27	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

RESULTS

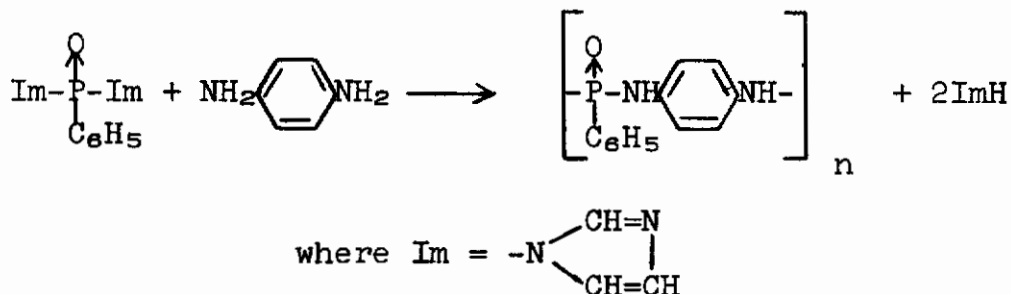
Preparation of Polymers

The reaction of suitable difunctional phosphorus compounds with diamines was used to form polymers. Thus, a dichlorophosphorus compound (e.g., phenylphosphonic dichloride) was reacted with 1,6-hexanediamine in the presence of a neutralizing agent such as sodium hydroxide or pyridine.



This method was used with several variations: reaction in an anhydrous medium with a homogeneous neutralizer such as triethylamine or with a dispersed phase neutralizer such as sodium hydride, and reaction in a two-phase (interfacial) system using aqueous sodium hydroxide as the neutralizer. The last variation, which has been investigated in detail by Wittbecker and Morgan¹ using reactants not containing phosphorus, was successful with aliphatic and aryl-aliphatic diamines. With aromatic diamines, however, polymer formation was precluded by preferential reaction of the dichloro compound with water.

Another method which proved useful for aromatic diamines involved transamination: heating a diimidazolyl phosphorus compound with a diamine caused release of the imidazole and formation of the polymer. This approach has been pursued by Staab² and co-workers in preparing nonpolymeric materials.



Typical polymers and their properties are listed in Table 1.

Properties of Polymers

As shown in Table 1, the various polymers varied widely in softening point and decomposition point. In general, the polymers from aliphatic diamines had low softening points and decomposed below 325°C. Those containing aromatic moieties softened at higher

Table 1.

Polyamides Containing Phosphorus

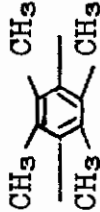
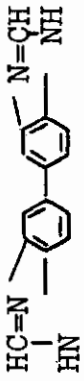
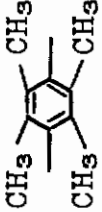
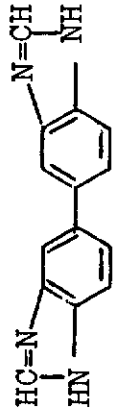
Phosphorus Compound	Diamine	Method ¹	Yield	Visc. η_{inh}	Soft. Pt., °C.	Decomp. Pt., °C.
$C_6H_5P(O)Cl_2$	$NH_2(CH_2)_6NH_2$	A	93	0.14^2	90-100	300
$C_6H_5P(O)Cl_2$	$NH_2(CH_2)_6NH_2$	B	42	0.05		
"	$C_4H_9NH(CH_2)_6NH_2$	A	61	0.04	75	320
"	$NH_2(CH_2)_3NH_2$	A	34	0.03	60	260
"	$NH_2(CH_2)_3O(CH_2)_3NH_2$	A	62	0.10^3	60	260
"	$NH_2(CH_2)_3NH(CH_2)_3NH_2$	A	50	0.03	70	295
"	$NH_2(CH_2)_2NH(CH_2)_2NH_2$	A	11		100	285
"	$NH_2CH_2C_6H_4CH_2NH_2$	A	48	0.06	120	270
"	$NH_2C_2H_4$ 	A	96	0.15	210	320
"		B	94		280	275
$C_6H_5P(S)Cl_2$	$NH_2(CH_2)_6NH_2$	A	75	0.05	80	225
$C_6H_5OP(O)Cl_2$	$NH_2(CH_2)_6NH_2$	A	95	0.17^4	70	325
"	$NH_2C_2H_4$ 	A	100	0.21	170	325

Table 1. (Contd.)

Phosphorus Compound	Diamine	Method ¹	Yield	Visc. inh	Soft. Pt., °C	Decomp. Pt., °C
$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{P}(\text{O})\text{Cl}_2$		B	100	0.02	> 440	430-450
$(\text{C}_6\text{H}_5)_2\text{NP}(\text{O})\text{Cl}_2$	"	B	16		> 430	430
$(\text{C}_6\text{H}_5)_2\text{NPCl}_2$	"	B	28		225	320
$\text{C}_6\text{H}_5\text{P}(\text{O})\text{Im}_2$	$\text{NH}_2(\text{CH}_2)_6\text{NH}_2$	C	35	0.08	80-85	250
$\text{C}_6\text{H}_5\text{P}(\text{O})\text{Im}_2$	$\text{NH}_2\text{C}_6\text{H}_4\text{NH}_2$	C	83	0.05	245-255	350
"	$\text{NH}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{NH}_2$	C	67	0.07	185-190	370-390
"	$\text{NH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{NH}_2$	C	77		210-215	330
"	$\text{HN} \begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \text{CH}_2-\text{CH}_2 \end{array} \text{NH}$	C	51	0.08	185-190	210
"	$\text{C}_6\text{H}_5\text{NHC}_6\text{H}_4\text{NHC}_6\text{H}_5$	C	No reaction			

¹ Methods A - Two-phase (interfacial) condensation
B - Anhydrous condensation
C - Transamination

² Ebulliometric molecular weight: 2600

³ Ebulliometric molecular weight: 1285

⁴ Ebulliometric molecular weight: 2160

temperatures and were more stable. For example, 4,4'-methylene-dianiline gave a polymer softening at 185-190°C. and decomposing at 370-390°C.

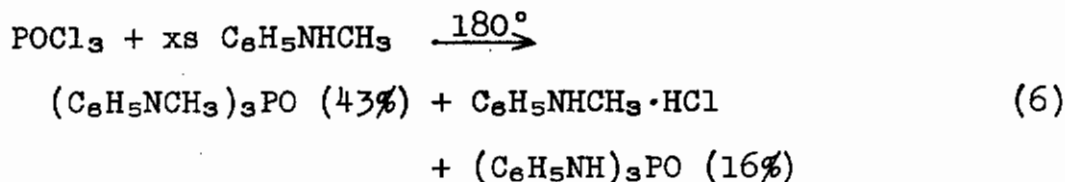
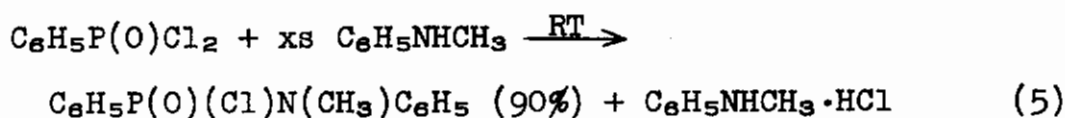
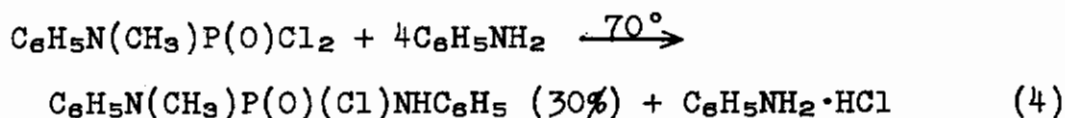
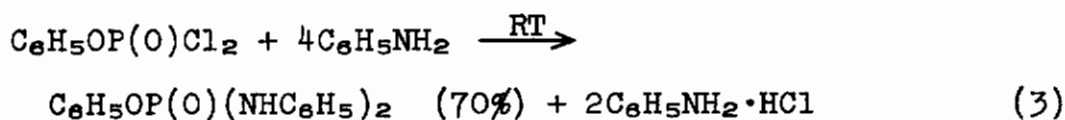
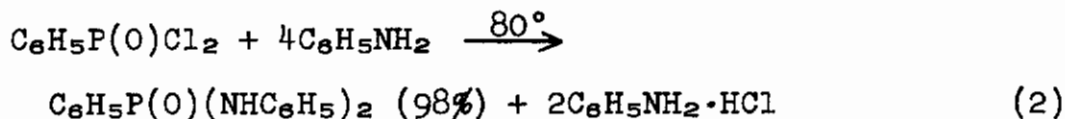
The most stable polymers were those prepared from 5,5'-bibenzimidazole, which did not soften at their decomposition points, 430-450°C.

Based on their viscosities, it appears that the degree of polymerization of all these polymers was low. This was also shown in some instances by ebulliometric molecular weight determinations.

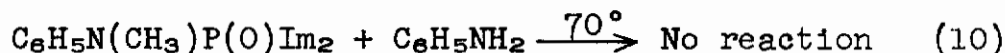
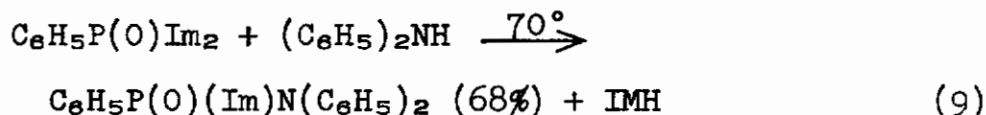
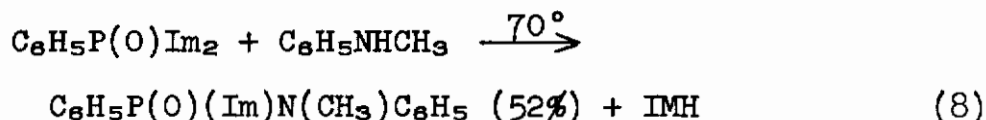
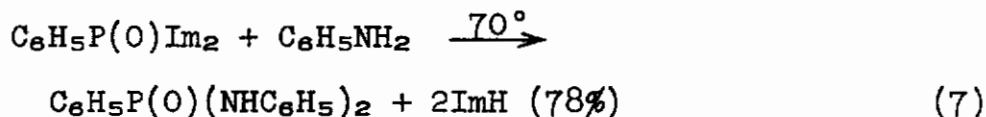
Model Reactions and Compounds

Prototype condensations were conducted with monofunctional reactants to learn something about the problems that would be encountered in polymer-forming reactions. Incomplete reactions or reactions involving undesirable by-products are undesirable in forming condensation polymers.

Thus, the reaction of various chlorophosphorus compounds with aromatic amines proceeded as follows:



In reaction (4) the phosphoramidic chloride appears relatively unreactive compared to nonamidic chlorides (cf. reactions (2) and (3)). This is attributed to the ability of the N-methylanilido radical to reduce the positive character of the phosphorus atom. This is further illustrated in the following transamination reactions:



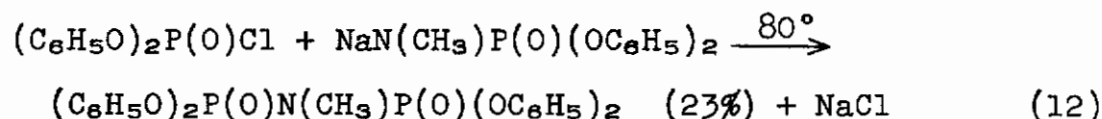
In reaction (8) substitution by one N-methylanilido group reduced the positive character of phosphorus atom to such an extent that no further substitution occurred. The same was true in reaction (9). In the absence of the N-methylanilido group, disubstitution took place, as indicated in reaction (7).

The use of sodium derivatives in preparing amides appears promising. In comparison with reaction (6), the use of a sodium amide derivative gave a better yield of the triamide:

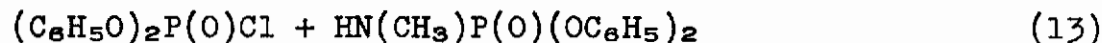


Also, the formation of N,N',N''-phenylphosphoric triamide was not encountered in the latter reaction.

Another successful use of an N-sodium derivative was:



The analogous reaction of the free amide did not go:



Model compounds have been used to compare the relative stability of chemical bonds. Table 2 lists a series of such compounds, one of which decomposes above 500°C.

Table 2.

Thermal Stability of Model Compounds

	<u>Decomp. Pt., °C.</u>
$\text{C}_6\text{H}_5\text{P}(\text{O})(\text{NHC}_6\text{H}_5)_2$	210
$\text{C}_6\text{H}_5\text{P}(\text{O}) \begin{array}{l} \text{N}(\text{CH}_3)\text{C}_6\text{H}_5 \\ \text{Im} \end{array}$	> 460
$\text{C}_6\text{H}_5\text{P}(\text{O}) \begin{array}{l} \text{N}(\text{C}_6\text{H}_5)_2 \\ \text{Im} \end{array}$	> 500

New Compounds

New compounds prepared under this contract are listed in Table 3. X-ray diffraction data for many of these compounds have been submitted for publication.

Table 3.

New Compounds Prepared

<u>Compound</u>	<u>m.p., °C</u>	<u>b.p., °C/mm</u>
Disodium phenylphosphonate dihydrate		
Monosodium phenylphosphonic acid		
N-1,3-Propanediamine phenylphosphonamidic acid	248-50	
N-1,3-Diamino-2-propanol phenylphosphonamidic acid	204-7	
1,2-Propanediamine salt of phenylphosphonic acid	214-17	
1,2-Propanediamine salt of phenylphosphonic acid, 1.5-hydrate	194-8	
1,3-Propanediamine salt of phenylphosphonic acid, 1.5-hydrate	238-42	
1,3-Diamino-2-propanol salt of phenylphosphonic acid	217-21	
N-Cyclohexyl phenylphosphonamidic acid	235-55	

Table 3. (Contd.)

<u>Compound</u>	<u>m.p., °C.</u>	<u>b.p., °C/mm</u>
1,3-Diethyl-2-phenyl-2-oxo-1,3,2-diazaphospholidine		155-75/2.5
N,N'-Dicyclohexyl methylphosphonothionic diamide	117-19	
Piperazine bis(phenylphosphonochloridic acid)	110-20	
N,N'-Dicyclohexyl phenylphosphonic diamide	164-7	
N-Methyl-N-phenyl-N'-phenylphosphorodiamidic chloride	162-3	
N,N'-Dicyclohexyl-N"-methyl-N"-phenylphosphoric triamide	97-8	
N,N'-Dicyclohexyl-N",N"-dimethylphosphoric triamide	103-4	
N-Methyl-N-phenyl-P-phenylphosphonamidic chloride	40	
N-Cyclohexyl-N'-methyl-N"-phenyl-phenylphosphonic diamide	123-4	
Bis(1-imidazolyl)-phenylphosphine oxide	98-100	
P,P-Bis(1-imidazolyl)-N-Methyl-N-phenylphosphinic amide	122-3	
N,N'-Dicyclohexyl-phenylphosphonic diamide	162-4	
N,N'-Dimethyl-2,2,3,3,4,4-hexafluoro-1,5-diaminopentane	80-4	
N,N'-Dicyclohexyl-1,4-diaminocyclohexane	82-5	
P-1-Imidazolyl-N,N-diphenyl-P-phenylphosphinic amide	170-174	
P-1-Imidazolyl-N-methyl-N-phenyl-P-phenylphosphinic amide	108-120	
Hexaphenylphosphorous triamide	281-7	

Table 3. (Contd.)

<u>Compound</u>	<u>m.p., °C.</u>	<u>b.p., °C/mm</u>
Diphenylphosphoramidous dichloride	40-41	
Sodium diphenylamide monoammoniate		
5,5'-Bibenzimidazole	280-3	

SUMMARY

New phosphorus polyamides containing the bibenzimidazole moiety showed decomposition points of 425-450°C. (797-842°F.) and did not soften below this temperature. The molecular weights, as indicated by viscosities, were low. One model compound, P-1-imidazolyl-N,N-diphenyl-P-phenylphosphinic amide, showed a decomposition point of about 500°C (932°F.).

REFERENCES

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2. Staab, H. A., Chem. Ber., 89, 1927 (1956).

PART II. P-C-P POLYMERS

J. R. Van Wazer, D. C. Bisno, George Brautigam, J. R. Brennan, G. M. Burch, C. F. Callis, M. M. Crutchfield, D. R. Dyroff, S. J. Fitch, L.C.D. Groenweghe, H. K. Hofmeister, R. R. Irani, S. K. Liu, David Matula, Ludwig Maier, Kurt Moedritzer, Gary Roth, H. E. Ulmer, J. T. Yoder

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INTRODUCTION

Theoretical considerations indicate that molecular stability with respect to breaking and making of bonds can be divided into two categories:

a. Reaction of a compound with its environment with concomitant reduction in the over-all free energy at the temperature under question.

b. Structural reorganization in which neighboring molecules which are identical or belong to the same chemical family react with each other by exchange of individual ligands.

The widely accepted opinion that high values of bond energies in polymers will lead to good thermal stability is not correct for either reaction with the environment or structural reorganization. Instead of bond energies, however, the important factors with respect to the thermal stability are the activation energies and free energies of the reactions responsible for thermal degradation. Based on studies of the rate of reorganization of various ligands attached to triply and quadruply connected phosphorus atoms, it was concluded that quadruply connected structures with P-C-P linkages should exhibit a higher thermal stability than the majority of other phosphorus compounds. As a result, considerable effort has been spent on the preparation, separation and evaluation of such types of structures. Major difficulties have been encountered in forming the essential P-C-P bridge in polymers, a problem which has not yet been solved to any degree of satisfaction in spite of the study of many different, apparently promising synthetic approaches. Because it has not been possible to prepare and separate satisfactorily a pure polymer with P-C-P backbone, efforts have also been directed toward the preparation of dimers and trimers, the thermal stability of which would be a good indication of what can be expected from the longer polymers themselves. Thus, it was found that tetrasodium methylenediphosphonate $\text{[NaO)}_2\text{P(O)-CH}_2\text{(O)P(ONa)}_2\text{]}$ was stable up to 500°C in a nitrogen atmosphere and up to 400°C in air. This result has been very encouraging to the research directed toward the preparation of P-C-P polymers.

In phosphorus chemistry, the more stable compounds are based on either a triply connected or quadruply connected phosphorus. Let us assume that the compound PX_3 (or alternately, say, OPX_3) undergoes structural reorganization with the compound PY_3 (or alternately OPY_3). In this case, the intermediate compounds PX_2Y and PXY_2 are formed. All of the multitude of reorganization reactions involving compounds from the group PX_3 , PX_2Y , PXY_3 , and PY_3 to give other compounds in this group can be derived from the following pair of equations for which equilibrium constants are given.



$$K_1 = (PX_3)(PXY_2)/(PX_2Y)^2 \quad (2)$$



$$K_2 = (PY_3)(PX_2Y)/(PXY_2)^2 \quad (4)$$

It has been shown mathematically¹ that K_1 and K_2 will equal $1/3$ if the X's and Y's exchange with each other in a completely random manner. Examples of reorganization in phosphorus chemistry have been the subject of a recent series of papers from this laboratory.^{1,2,3,4,5}

When X is chosen to be a monofunctional ligand (e.g. a chlorine atom) and Y a difunctional ligand (e.g. a bridging oxygen atom), the POX_2Y , $POXY_2$, and POY_3 groupings do not represent molecules but are parts of molecules--end groups, middle groups, and branch groups, respectively, making up polyphosphorus structures. It is quite obvious that these structural building units can never appear independently and must always be connected together in the form of molecules, so that equations 1 and 3 then represent only part of the over-all reorganization process--that part involving only change in functionality of a building unit. The true reorganization consists of the concomitant action of this change of functionality with a process which is mathematically equivalent to the sorting or reshuffling of these building units between and within molecules. Completely random reshuffling can be treated mathematically.

Although kinetic studies have not previously been carried out on the rates of reorganization, approximate values of these rates were obtained. Examples of this type of work are the following: The phosphorus trihalides show detectable reorganization at room temperature fifteen minutes after being mixed. Equilibrium appears to be reached in less than a week at room temperature. Correspondingly, the oxyhalides or thiohalides reorganize much more slowly at room temperature; but, at $265^\circ F.$, detectable reorganization is found in about an hour, with equilibrium being achieved in less than a week. Reorganization of methyldichlorophosphine to give the equilibrium mixtures of PCl_3 ,

$(\text{CH}_3)\text{PCl}_2$, $(\text{CH}_3)_2\text{PCl}$, and $(\text{CH}_3)_3\text{P}$ is so slow at 450°F . that no chemical change could be detected after 65 hours, with equilibrium taking much longer. However, at 575°F ., equilibrium is achieved in 65 hours. At this same temperature, methylthionophosphonic dichloride shows no appreciable reorganization.

From these types of studies, several broad conclusions were made: First, it appears that the rate of reorganization of various bonds to phosphorus lie in the following order:



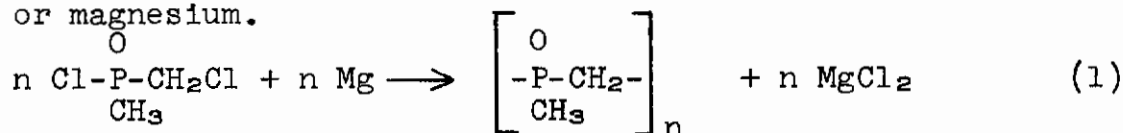
Secondly, bonds to triply connected phosphorus reorganize much faster than bonds to quadruply connected phosphorus. This means that chain structures based on $\text{P} - \text{C} - \text{P}$ linkages, with the phosphorus being quadruply connected, should exhibit a higher order of thermal stability than the majority of compounds based on either carbon or phosphorus.

DISCUSSION

This research included a number of different attacks on the general problem of producing polymeric structures containing phosphorus. Among them are studies of compounds of the following types: $\text{P} - \text{C} - \text{P}$, $\text{P} - \text{C} - \text{S} - \text{P}$, $\text{P} - \text{C} - \text{O} - \text{P}$, polyphosphinates, polyphosphines, phosphonium salts, phosphosilicones, $\text{P} - \text{N} - \text{C} - \text{P}$ polymers, and $\text{P} - \text{B}$ polymers.

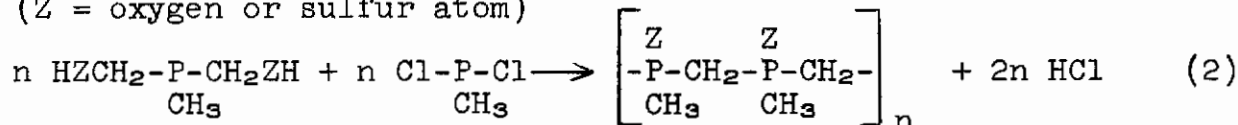
P-C-P Type Polymers

A satisfactory method for making polyphosphine oxides or sulfides has not been found. The most promising reaction is the condensation of methyl, chloromethylphosphinic chloride with zinc or magnesium.



However, a pure low molecular weight polymer could not be separated out of the reaction mixture in spite of considerable effort in this direction.

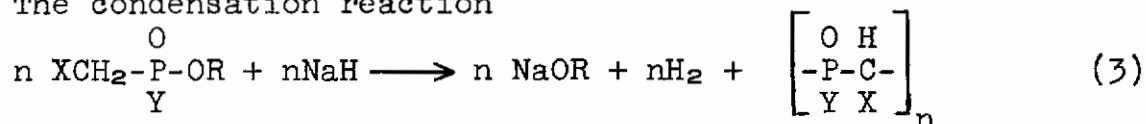
Various other approaches to obtain this type of polymer were not successful. These include the following reactions: (Z = oxygen or sulfur atom)



Methyl, bishydroxymethylphosphine and methyldichlorophosphine reacted to give mixtures of monomeric quadruply connected phosphorus compounds, whereas methyl, bishydrothiomethyl-

phosphine could not be prepared.

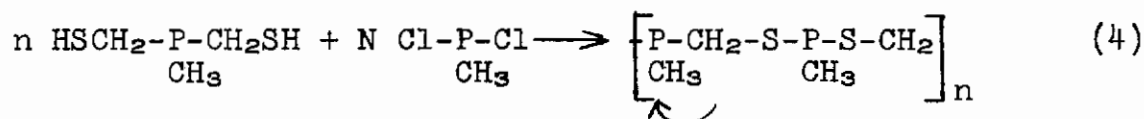
The condensation reaction



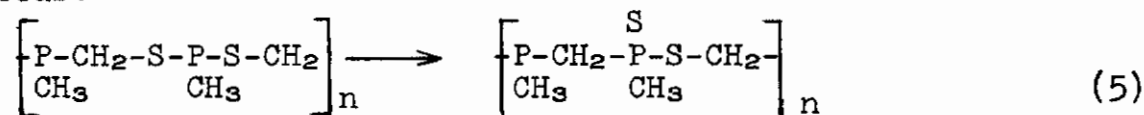
in which R = alkyl or aryl group, X = H or R and Y = R or OR was investigated. Various reaction products were obtained in complicated mixtures and definite proof of the presence of even small amounts of the desired structures could not be obtained.

P-C-S-P Polymers

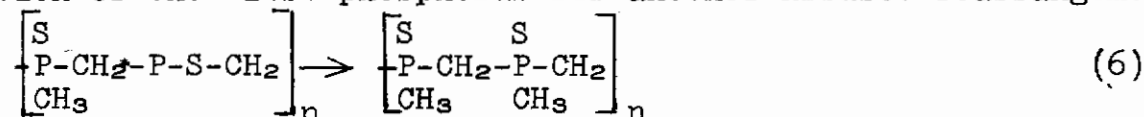
By reacting methyl, bishydrothiomethylphosphine with methyl-dichlorophosphine, a P-S-C-P type polymer can be expected to form:



Upon heating, an Arbusov type rearrangement can be expected to occur:



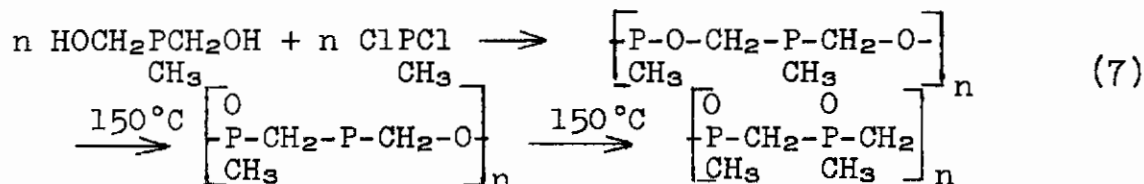
The sulfur in the nonbridging position is attached to a phosphorus connected to two carbon atoms and one other sulfur. According to previous findings, it would be expected that this sulfur will be attracted by the triply connected phosphorus atoms which are bonded to three carbon atoms, thus freeing the isolated position of the first phosphorus for another Arbusov rearrangement:



A major problem in this scheme is the preparation of the starting material methyl, bishydrothiomethylphosphine. Although methyl bis(hydroxymethyl)phosphine was easily prepared from methyl phosphine, the preparation of the analogous compound, methyl bis(hydrothiomethyl)phosphine was unsuccessful.

P-C-P Polymers by Reorganization of PCOP Linkages

It was expected, from chemical analogy, that the reactions

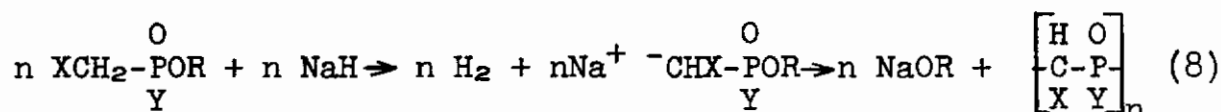


would proceed, one of the oxygens migrating over a carbon and a phosphorus atom to the isolated position. It is known⁶ that the P-O bond breaks easily at 150°C.

The hydrogen n-m-r spectra of the product showed that the expected P-CH₂-P grouping was not present.

Polyphosphinates

The reaction of sodium hydride with phosphonate esters might be expected to be analogous to the acetoacetic ester condensation and proceed by the equation:



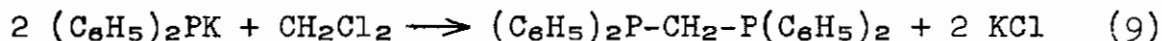
The proposed reaction seems to be workable with phosphonate esters to produce polyphosphinates. The following phosphonates were tried (X, Y and R in Reaction (12) are given)

<u>X</u>	<u>Y</u>	<u>R</u>
H	OCH ₃	CH ₃ (three attempts)
Cl	OC ₂ H ₅	C ₂ H ₅
PO ₃ (C ₂ H ₅) ₂	OC ₂ H ₅	C ₂ H ₅
H	OC ₄ H ₉	C ₄ H ₉ (two attempts)
C ₆ H ₅	OC ₂ H ₅	C ₂ H ₅

In each case, the desired reaction was aborted through loss of reactants as insoluble ester-salts. Minor amounts of new materials have been detected, but could not be separated, and the approach has been abandoned.

Polyphosphines

The successful utilization of the reaction described in the literature to give the diphosphine (C₆H₅)₂PCH₂P(C₆H₅)₂:



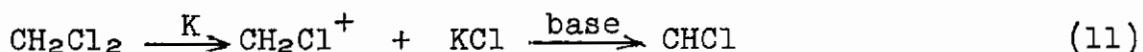
prompted us to study the application of this type of reaction to the synthesis of polymers according to the following equation.



When the above reaction was run in dioxane as solvent, it was found, however, that only about 34% of the Cl available in methylenedichloride could be detected as KCl in the insoluble residue of the reaction product. The P³¹ n.m.r. spectrum of the concentrated dioxane solution containing the reaction product showed about 10 peaks in the range -50 to -7 ppm. No efforts have been

made to separate the various products.

One of the reasons for the failure of this research seems to be the intermediate formation of a carbene,

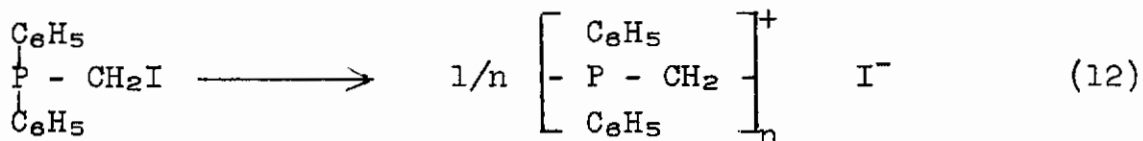


which may enter several side reactions with the present phosphorus compounds. Such a reaction is favored by a basic reaction medium as is the case in solutions of dipotassium, phenylphosphine.

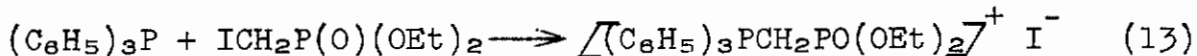
Intermediate carbene formation could very well be the reason for several other unsuccessful reactions using methylene dichloride or its derivatives in basic media for syntheses, e.g., $\text{CH}_2\text{Cl}_2 + \text{NaPO}(\text{OEt})_2$, and $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{Cl} + \text{KP}(\text{C}_6\text{H}_5)_2$.

Phosponium Salts

The principle of the phosponium salt formation applied to a phosphorus compound containing the iodomethyl group and the lone electron pair of a triply connected phosphorus atom in one molecule should yield polymeric structures.

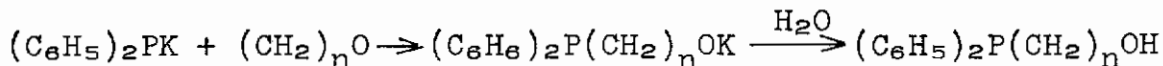


A model reaction has shown that an iodomethyl group directly attached to phosphorus quaternizes easily with triphenylphosphine.

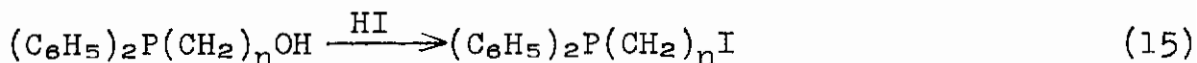


The quaternized product gave a P^{31} n.m.r. shift (-22.2 ppm) which is typical for triphenylphosphonium salts: $(\text{C}_6\text{H}_5)_3\text{CH}_3\text{P}^+ \text{I}^-$ gives -21.0 ppm. Since only one peak was obtained, it must be concluded that the other phosphorus atom in the molecule, the "phosphonate" phosphorus, has its n.m.r. peak at about the same position and thus causes an overlap of the two resonances.

An intermediate for the monomer starting material was prepared according to a procedure which has been reported in the literature for $n = 2$:

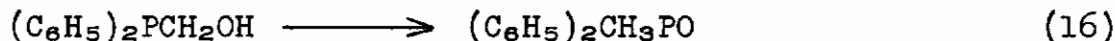


The resulting hydroxyphosphine should be converted to the corresponding iodocompound. (14)



which is expected to quaternize as stated above.

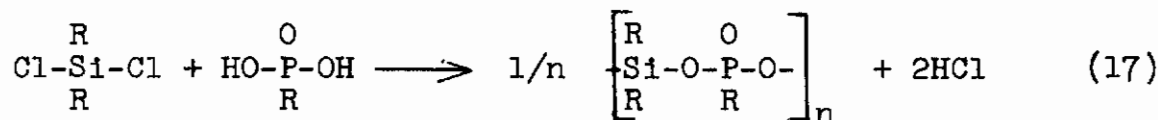
The reaction product according to reaction 41 for $n = 2$ proved to be the β -hydroxyphosphine as indicated by its P^{31} n.m.r. shift of +22.9 ppm. The corresponding compound for $n = 1$ which was obtained from potassium, diphenylphosphine and paraformaldehyde gave an n.m.r. peak at -29.8 which would be consistent with a phosphine oxide structure: e.g. $(C_6H_5)_2(CH_2Cl)PO$:



had occurred.

Phosphosilicones.

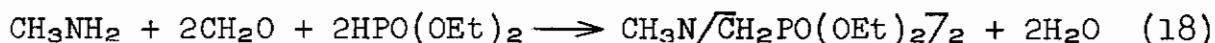
The exceptional thermal and hydrolytic stability of silicones suggested the synthesis of structures in which every second silicon atom was substituted by phosphorus. The best suitable approach seemed to be the elimination of HCl from equimolar amounts of a phosphonic acid and a dialkyl or diaryldichlorosilane.



The products obtained for $R = CH_3$ and C_6H_5 were viscous liquids or low-melting solids. For $R = CH_3$, the polymer appears to be quite stable in cold water, but hydrolyzes readily in boiling water to form methylphosphonic acid and silicone oil. The compound for which $R = C_6H_5$ hydrolyzes after only several minutes of boiling in water forming phenylphosphonic acid and a white solid silicone.

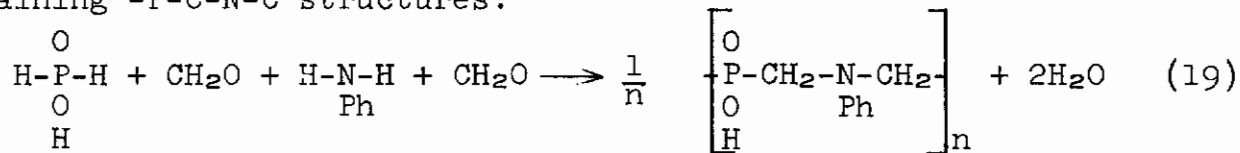
P-C-N-P Polymers

As a model compound for this new type of polymer based on the P-C-N-P-backbone, the following ester has been synthesized according to a procedure in the literature⁷:



Hydrolysis of the ester with concentrated hydrobromic acid gave the acid $(HO)_2OP-CH_2-N(CH_3)-CH_2-PO(OH)_2$ which was tested for thermal stability.

A similar approach was used in a preparation of a material containing -P-C-N-C structures:



The above reaction product separated as yellow jellylike material which on drying at 120°C turns into a brown solid in-

soluble in all common solvents. The thermal stability of this material was lower than expected, with decomposition occurring at about 200-250°C. Apparently, substitution of a N for every second P atom in a P-C-P chain does not favorably influence the thermal stability of the material.

Phosphorus-Boron Polymers

In 1891 Moissan reported⁸ that the reaction between white phosphorus and boron triiodide in carbon disulfide gives a product of the composition BPI₂. This material might be considered as a fortuitous mixture except for the fact that it is slightly volatile at its melting point and gives a crystalline sublimate. Moissan also reported that BPI₂ can be reduced in hydrogen to BPI. Unfortunately, he gave very sparse experimental details, and no additional work on these compounds has been reported in the literature.

Moissan's preparation of BPI₂ was repeated using carefully purified reagents and with the strict exclusion of oxygen and moisture. The reported color changes were observed, but the red solid product was not volatile in high vacuum at 225°C, which is well above Moissan's reported sublimation temperatures. The small amount of orange sublimate which did collect was reacted with phenyllithium to convert it to a more easily handled derivative, but biphenyl was the only product which could be isolated from this reaction.

Alkylation and Arylation Reactions

The reactions of a number of halogen compounds with organo-metal compounds were followed by means of n.m.r. analysis. The results are summarized in the following tables.

Table 1.

Alkylation of Phosphorus Compounds with Pb(CH₃)₄, Dissolved
in Toluene (85% Solution)

<u>P-Compound</u>	<u>Ratio P-Comp. :Pb(CH₃)₄</u>	<u>Heating Time at 125°C in hours</u>	<u>Products</u>	<u>Yield%</u>
PCl ₃	2.1:1	20	CH ₃ PCl ₂	100 ^a
CH ₃ PCl ₂	2.2:1	20	(CH ₃) ₂ PCl	^b
CH ₃ PBr ₂	2.5:1	1(22°C)	(CH ₃) ₂ PBr	13 ^c
C ₆ H ₅ PSCl ₂	2.3:1	120	C ₆ H ₅ (CH ₃)PSCl	90
CH ₃ PSCl ₂	2.5:1	200	(CH ₃) ₂ PSCl	81

Table I (Contd.)

P-Compound	Ratio P-Comp. :Pb(CH ₃) ₄	Heating Time at 125°C in hours	Products	Yield %
(CH ₃) ₂ PSCl	2.5:1	200	(CH ₃) ₃ PS	12
C ₆ H ₅ POCl ₂	2.3:1	200	C ₆ H ₅ (CH ₃)POCl	19

^aAfter 4 hours heating at 122°C, 86% CH₃PCl₂ had formed.

^bN.m.r. peak intensity decreased strongly (indication of extensive decomposition of phosphorus-compound). After 4 hours heating at 122°C, 12% of the expected (CH₃)₂PCl had formed and the n.m.r. peak intensity was strong.

^cThe content of the tube turned solid after one hour standing at room temperature, probably caused by formation of phosphonium type (R₃PBr⁺)Br⁻ compounds.

Table 2.

Alkylation of Phosphorus Compounds with Pb(C₂H₅)₄

P-Compound	Ratio P-Comp. :Pb(C ₂ H ₅) ₄	Heating Time at 125°C in hours	Products	Yield%
PBr ₃	2.79:1	19 (22°C)	C ₂ H ₅ PBr ₂	60 ^a
CH ₃ PBr ₂	2.71:1	2	CH ₃ C ₂ H ₅ PBr	100 ^a
PCl ₃	2.56:1	4	C ₂ H ₅ PCl ₂	100
PCl ₃	1.87:1	4	C ₂ H ₅ PCl ₂ (C ₂ H ₅) ₂ PCl	89 11
CH ₃ PCl ₂	1.84:1	4 ^b	CH ₃ C ₂ H ₅ PCL	100
C ₆ H ₅ PCl ₂	1.96:1	4	C ₂ H ₅ (C ₆ H ₅)PCl	100
(CH ₃) ₂ PCl	1.85:1	66	(CH ₃) ₂ C ₂ H ₅ P (CH ₃)(C ₂ H ₅) ₂ P (CH ₃) ₃ P	83.5 8.5 ^c 8.5 ^c
(C ₆ H ₅) ₂ PCl	2.07:1	66	(C ₆ H ₅) ₂ C ₂ H ₅ P C ₆ H ₅ (C ₂ H ₅) ₂ P (C ₆ H ₅) ₃ P	90 5 ^d 5 ^d

Table 2. (Contd.)

<u>P-Compound</u>	<u>Ratio P-Comp. :Pb(C₂H₅)₄</u>	<u>Heating Time at 125°C in hours</u>	<u>Products</u>	<u>Yield%</u>
PSCl ₃	2.734:1	39	C ₂ H ₅ PSCl ₂ (C ₂ H ₅) ₂ PSCl	92 8
CH ₃ PSCl ₂	1.84:1	66(115°C)	CH ₃ C ₂ H ₅ PSCL	77 ^e
C ₆ H ₅ PSCL ₂	1.92:1	66(115°C)	C ₂ H ₅ (C ₆ H ₅)PSCl (C ₂ H ₅) ₂ (C ₆ H ₅)PS	70 ^f 20
(CH ₃) ₂ PSCl	1.89:1	130	(CH ₃) ₂ C ₂ H ₅ PS	84
POCl ₃	2.64:1	90	C ₂ H ₅ POCl ₂ (C ₂ H ₅) ₂ POCl	40 20
ClCH ₂ POCl ₂	1.87:1	160	C ₂ H ₅ (ClCH ₂)POCl	42
C ₆ H ₅ POCl ₂	1.77:1	120	C ₂ H ₅ (C ₆ H ₅)POCl	50

^aIt is better to carry out this reaction in an open flask, since the formation of phosphonium salts can be avoided in this way.

^bFurther heating of the tube for 17 hours at 125°C caused strong decomposition of the product.

^cProducts formed by reorganization of (CH₃)₂C₂H₅P to give CH₃(C₂H₅)₂P plus (CH₃)₃P. Additional heating for 117 hours at 125°C gave 67% of (CH₃)₂C₂H₅P, 16.5% of CH₃(C₂H₅)₂P and 16.5% of (CH₃)₃P. PbCl₂ might act as a catalyst in this reorganization reaction.

^dProducts formed by reorganization of (C₆H₅)₂C₂H₅P to give C₆H₅(C₂H₅)₂P plus (C₆H₅)₃P (see c).

^eAdditional heating of the tube for 70 hours at 125°C gave 58% of CH₃C₂H₅PSCL and 35% of CH₃(C₂H₅)₂PS.

^fAdditional heating of the tube for 70 hours at 125°C gave 47% of C₂H₅(C₆H₅)₂PSCl and 44% of (C₂H₅)₂C₆H₅PS.

Table 3.

Arylation of Phosphorus Compounds with $\text{Pb}(\text{C}_6\text{H}_5)_4$

<u>P-Compound</u>	<u>Ratio P-Comp.: $\text{Pb}(\text{C}_6\text{H}_5)_4$</u>	<u>Heating Time at 180°C in hours</u>	<u>Products</u>	<u>Yield%</u>
PBr_3	3.01:1	180	$\text{C}_6\text{H}_5\text{PBr}_2$ $(\text{C}_6\text{H}_5)_2\text{PBr}$	68 21
CH_3PBr_2	4.63:1	180	$\text{C}_6\text{H}_5\text{PBr}_2$ $\text{CH}_3\text{C}_6\text{H}_5\text{PBr}$	54 ^a 7
PCl_3	3.03:1	180	$\text{C}_6\text{H}_5\text{PCl}_2$ $(\text{C}_6\text{H}_5)_2\text{PCl}$	93 2
CH_3PCl_2	2.01:1	39(165°C)	$\text{C}_6\text{H}_5\text{PCl}_2$ $\text{CH}_3(\text{C}_6\text{H}_5)\text{PCl}$	55 ^b 20
$\text{C}_6\text{H}_5\text{PCl}_2$	3.0:1	83	$(\text{C}_6\text{H}_5)_2\text{PCl}$	90
$(\text{CH}_3)_2\text{PCl}$	2.03:1	39(165°C)	$\text{CH}_3(\text{C}_6\text{H}_5)_2\text{P}$ $(\text{CH}_3)_2\text{C}_6\text{H}_5\text{P}$	50 ^c 50
$(\text{C}_6\text{H}_5)_2\text{PCl}$	2.98:1	180	$(\text{C}_6\text{H}_5)_3\text{P}$	95
PSCl_3	3.0:1	180	$\text{C}_6\text{H}_5\text{PSCl}_2$ $(\text{C}_6\text{H}_5)_2\text{PSCl}$	35 32
CH_3PSCl_2	1.9:1	66	$\text{CH}_3\text{C}_6\text{H}_5\text{PSCl}$	100
$\text{C}_6\text{H}_5\text{PSCl}_2$	2.1:1	136	$(\text{C}_6\text{H}_5)_2\text{PSCl}$ $(\text{C}_6\text{H}_5)_3\text{PS}$	94 6
$\text{ClCH}_2\text{PSCl}_2$	1.9:1	180	$\text{ClCH}_2(\text{C}_6\text{H}_5)\text{PSCl}$	46
POCl_3	3.01:1	180	$\text{C}_6\text{H}_5\text{POCl}_2$ $(\text{C}_6\text{H}_5)_2\text{POCl}$	29 15.5
$\text{C}_6\text{H}_5\text{POCl}_2$	1.93:1	66	$(\text{C}_6\text{H}_5)_2\text{POCl}$	68
$\text{ClCH}_2\text{POCl}_2$	2.0:1	180	$\text{ClCH}_2(\text{C}_6\text{H}_5)\text{POCl}$	11

^a CH_3PBr_2 decomposes partly at this temperature to give PBr_3 and other products. PBr_3 then reacts with $\text{Pb}(\text{C}_6\text{H}_5)_4$ to give $\text{C}_6\text{H}_5\text{PBr}_2$. When a tube was kept for 18 hours at 100°C, no $\text{C}_6\text{H}_5\text{PBr}_2$ was formed, but 17% of $\text{CH}_3\text{C}_6\text{H}_5\text{PBr}$ could be detected.

^b CH_3PCl_2 reorganizes partly at this temperature to give PCl_3 and other products. PCl_3 then reacts with $\text{Pb}(\text{C}_6\text{H}_5)_4$ to give $\text{C}_6\text{H}_5\text{PCl}_2$. When a tube was kept for 18 hours at 100°C, no reaction occurred.

^cCould have been formed from CH_3PCl_2 , a reorganization product of $(\text{CH}_3)_2\text{PCl}$.

Table 4.

Alkylation of Alkylhaloarsines with Tetraalkyllead Compounds

R in PbR ₄	Arsenic Compound	Product	Yield %	B.P. °C	n _D ²⁰
CH ₃	CH ₃ AsBr ₂	(CH ₃) ₂ AsBr	90	126-129	1.5703 ²⁶
C ₂ H ₅	CH ₃ AsBr ₂	CH ₃ (C ₂ H ₅)AsBr	80	154-155	1.5732
CH ₂ =CH	CH ₃ AsBr ₂	CH ₃ (CH ₂ =CH)AsBr	60.5	144-145	
C ₅ H ₉	CH ₃ AsBr ₂	CH ₃ (C ₄ H ₉)AsBr	57	172-178	1.6368
C ₂ H ₅	(CH ₃) ₂ AsBr	(CH ₃) ₂ (C ₂ H ₅)As	56	83-84	

d. Tetraphenyltin as Arylating Agent. Two experiments with tetraphenyltin demonstrated that it can also be used as an arylating reagent. Tetraethyltin was shown earlier to give excellent yields of C₂H₅PBr₂ when reacted with PBr₃⁹.

The results are summarized in Table 5.

Table 5.

Arylation of PCl₃ and PSCl₃ with Tetraphenyltin

P-Compound	Ratio P-Comp. :Sn(C ₆ H ₅) ₄	Heating Time at 180°C in Hours	Products	Yield %
PCl ₃	3.1:1	350	C ₆ H ₅ PCl ₂	65
PSCl ₃	3.09:1	130	C ₆ H ₅ PSCl ₂ (C ₆ H ₅) ₂ PSCl	58 36

Contrary to tetraphenyllead, tetraphenyltin reacted much faster with PSCl₃ than with PCl₃, e.g., while no product had been formed with PCl₃ after 40 hours heating with Sn(C₆H₅)₄ at 180°C, PSCl₃ gave under the same conditions 22% C₆H₅PSCl₂ and 36% (C₆H₅)₂PSCl. Since the content of the tube containing PCl₃ and Sn(C₆H₅)₄ in ratio 3.1:1 became nearly completely solid when cooled to room temperature after heating for 40 hours at 180°C, it is assumed that a complex of the type (PCl₂)₂⁺⁺ [Sn(C₆H₅)₄Cl₂]⁻⁻ is first formed which is subsequently decomposed, after long heating, to give C₆H₅PCl₂ and (C₆H₅)₂SnCl₂.

Proof of Structure by Means of Nuclear Magnetic Resonance

Methyl Phosphine Confirmation of the synthesis of methyl phosphine, H₂PCH₃, was provided by a proof of structure, utilizing

P^{31} n.m.r. at 24.3 Mc, H^1 n.m.r. at 40 and 60 Mc, and double resonance techniques. The compound provides an elegant example of the utilization of these techniques for structure proof.

The 24.3 Mc P^{31} n.m.r. spectrum of methyl phosphine exhibited three major peaks of relative intensity 1:2:1, separated by 187 cps. The chemical shift is +164.0 ppm relative to 85% H_3PO_4 . The over-all triplet structure is consistent with two hydrogen atoms bonded directly to phosphorus. For a first order spectrum, one would also expect each peak of this triplet to be split into a smaller 1:3:3:1 quartet by the three hydrogens of the methyl group, which should be less strongly coupled to the phosphorus nucleus. The spectrum showed that each peak of the triplet was actually composed of up to 10 peaks each in an asymmetrical pattern. This suggested that there was appreciable interaction between the methyl hydrogens and the phosphine hydrogens, and that the spectrum could not be explained by a simple first order analysis.

Additional information was provided by the H^1 n.m.r. spectrum at 60 Mc. It contained two bands separated by 190 cps. Moreover, the integrated spectrum showed that the band at lower field, a symmetrical quartet, accounted for only one hydrogen atom out of five. The complex band at higher field resulted from the four other hydrogen atoms. The symmetrical quartet arises from the splitting of $1/2$ the phosphine hydrogen resonance by the three methyl hydrogens. The other $1/2$ of the phosphine hydrogen resonance fell at the same energy level as the methyl hydrogen resonance, resulting in mixing of states and a complex spectrum. This provided an explanation for the unusual splitting in the 24.3 Mc phosphorus spectrum.

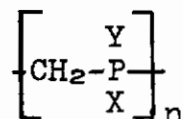
The H^1 spectrum was then taken at 40 Mc. Since the coupling (expressed in cps) between the hydrogens is independent, while the chemical shift is dependent on the radiofrequency used, overlapping bands were shifted, although it did not completely separate them. Double resonance experiments were then used to decouple phosphorus from hydrogen by irradiating with a second radiofrequency at 16.2 Mc and high power, while observing H^1 at 40 Mc and low power. This effectively removes the spin-spin coupling between hydrogen and phosphorus. The 187 cps splitting of the phosphine hydrogen signal was collapsed and the methyl and phosphine hydrogen resonance bands appeared separately. The resulting decoupled spectrum approximates first order hydrogen splitting and provides unequivocal confirmation of the structure of methyl phosphine. The small residual peaks that remain in the decoupled spectrum are due to a combination of insufficient power from the decoupler output and second order splitting due to the proximity of the decoupled bands.

Dimethyl Methylphosphonate Phosphonate esters ordinarily give poorly resolved broad resonances in P^{31} n.m.r. due to strong coupling to phosphorus of the protons on the carbon atoms nearest

to phosphorus, merged with weaker coupling of protons on the next nearest carbon atoms. Dimethyl methylphosphonate provides a special case in which there are only two kinds of protons ($\text{CH}_3\text{-P-}$ and $\text{CH}_3\text{OP-}$), and in which the coupling constants, $J_{\text{PH}_3} = 10.9$ cps and $J_{\text{PH}_3} = 17.3$ cps, can be accurately measured from proton n.m.r. spectra. Fortuitously, there is no overlap of the lines, and all twenty-eight of the lines predicted by simple first-order theory can be resolved in the P^{31} spectrum. The small molar volume of the compound is helpful in increasing the signal strength and thereby increasing the resolving power. The ninth and tenth lines from either end of the spectrum, having a separation of only 2.2 cps, provide a good measure of the resolving power of the instrument, and have proved useful in focusing the magnet for maximum resolving power.

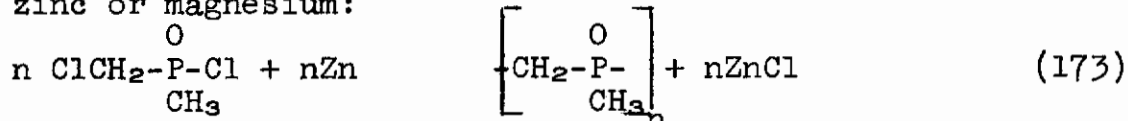
CONCLUSIONS

Experimental results show that phosphorus-containing polymers of the type



where Y = oxygen or sulfur and X = an alkyl, aryl, alkoxy or aryloxy group, can be expected to be stable at temperatures of 400°C or higher. Although model compounds have been made the thermal stability of which support this conclusion, the preparation of pure polymeric molecules of this type has not been achieved.

After two years of effort, the most promising reaction found was the polymerization of methyl, chloromethylphosphonic chloride with zinc or magnesium:



The presence of the desired $\text{P-CH}_2\text{-P}$ structure in the product thus obtained has been shown by n.m.r. spectroscopy. However, repeated attempts to separate out the polymeric material thus obtained, free from the strongly complexed zinc or magnesium chloride and free from undesirable by-products (such as phosphonium structures) have not succeeded.

The other approaches for the preparation of such polymers have either been giving extremely low yield of products which were difficult to identify or a completely different reaction occurred, sometimes producing a complicated mixture of unidentified compounds.

Since long-chain P-C-P polymers have not been produced, it is not possible to predict exactly which physical properties can be

expected from the finished polymer. Tensile strength, flexibility, elasticity, etc., are all properties which are specific for polymers exhibiting more than a certain minimum molecular weight and cannot be obtained by extrapolation of properties of shorter molecules.

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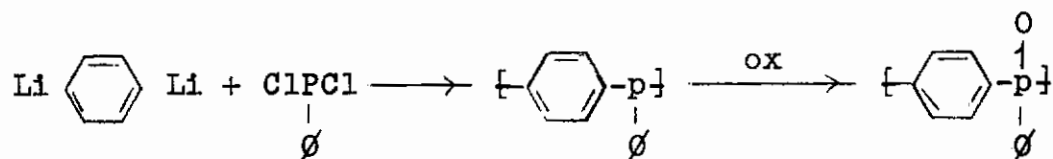
PART III. ORGANO-PHOSPHORUS POLYMERS

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INTRODUCTION

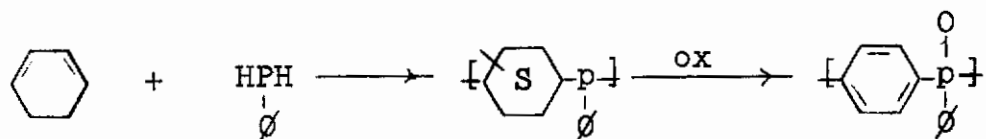
The work reported here was directed primarily to the preparation of poly phenyl p-phenylene phosphine oxide, since there was reason to believe that such a polymer would have a high level of thermal stability. Prior to undertaking this project we had attempted a "direct" synthesis of this structure via the reaction of p-dilithio benzene and phenyl dichlorophosphine.



This reaction was never successful in our hands because the dilithiobenzene preparation cannot be made pure and the "polymer" precipitated from the non-polar reaction solvent before any appreciable molecular weight was obtained.

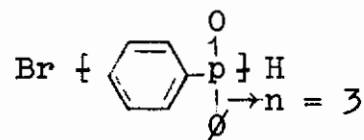
RESULTS AND DISCUSSION

We proposed to attempt the synthesis of the desired poly phenyl phenylene phosphine oxide by making use of the well-known addition of P-H bonds to carbon-carbon double bonds. The reaction proposed is shown below:



The reaction of 1,3-cyclohexadiene and phenyl phosphine did result in a polymer. However, the reaction is not as clear cut as represented since cyclohexene and some distillable phosphorus-containing compounds were also produced. The polymer contained a higher phosphorus content than expected and could not be dehydrogenated to any identifiable product.

During the course of this work we had occasion to repeat the reaction of bromobenzene, phosphorus trichloride and aluminum chloride reported by Davies and Mann¹. This reaction gives only a poor yield of p-bromophenyl dichlorophosphine of uncertain purity. We found by hydrolysis of the pot residue that the major product was actually a low polymer analyzing for the following structure:



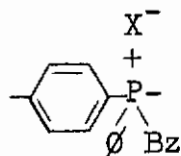
This material when examined by thermogravimetric analysis appeared to give two levels of decomposition; the higher one occurring at about 550°C.

It was evident, however, that we still did not have in our hands suitable methods of synthesis of the desired polymer. We decided to establish the level of thermal stability inherent in the p-phenylene phosphine oxide structure by synthesizing and testing suitable model compounds. To this end we prepared p-phenylene bis(diphenyl phosphine oxide) essentially by the methods reported by Baranauckas, Carlson, Harris and Lisanke². Using differential thermal analysis we found that this material decomposed at 450°C. This result is in agreement with the data obtained on the thermal stability of this compound by the previous workers². Furthermore, an examination of alkylene bis(diphenyl phosphine oxides) showed that they decomposed somewhat lower in the 400-445°C range.

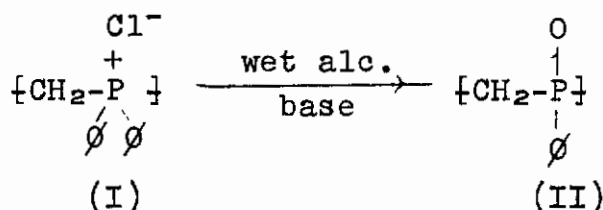
CONCLUSIONS

We conclude from this work that poly p-phenylene phosphine oxides would not be stable above 450°C and would not, therefore, fulfill the requirements of stability to 1000°F.

Two other points of interest should be mentioned although they do not relate directly to the objective of this work. The first of these concerns the elimination of phosphonium salts under basic conditions. We have found that the action of wet-alcoholic base on p-phenylene bis(triphenyl phosphonium iodide) gave at least a 75% yield of triphenyl phosphine oxide. This indicated that the phosphorus to phenylene linkage was broken preferentially in the reaction. Base cleavage of p-phenylene bis(diphenyl benzyl phosphonium iodide), however, gave p-phenylene bis(diphenyl phosphine oxide) as the isolable product. This may indicate that basic cleavage of a polymer of the following structure



would be an attractive method of preparing the desired poly phenyl p-phenylene phosphine oxide. Also, we observed that the action of base on an impure polymer (believed to have structure I below) gave a polymeric water soluble product whose infrared spectrum was compatible with that which might be expected of poly phenyl methylene phosphine oxide (II).



Product (II) was not "pure" and did not show stability above 300°C.

The second point of interest involves an unexpected reaction which we observed. Phosphorus halides and active metals such as magnesium or lithium are not known to react at ordinary temperatures. We have observed, however, that diphenyl chlorophosphine, magnesium (or lithium) and tetrahydrofuran react exothermally to give a good yield of diphenyl-4-hydroxybutyl phosphine. When the reaction is carried out on phenyl dichlorophosphine the product is phosphobenzene (e-P=P-e). All phosphorus halides give a reaction with active metals and tetrahydrofuran but in many cases, such as with phosphorus trichloride or phosphorus oxychloride, the products are complicated and have not been identified. We feel that this reaction deserves more attention and can be developed into another route to the preparation of compounds having phosphorus-carbon bonds.

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